

HYDROCRACKING OF COAL AND PETROLEUM OILS

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Abstract

Hydrocracking of coal-based oils needs higher hydrogen pressure when compared to petroleum oils and both types of oils affect almost similar naphtha yields of 77 to 80% at a pressure of 2000 p.s.i. and 500°C. Coal-based oils produce naphtha of superior quality but with higher hydrogen consumption. At about 80% yield, naphtha from coal oil had a clear research octane number of 88 with a hydrogen consumption of about 1550 cu. ft. per barrel of feed, whereas the product from gas oil has an octane number of 78 with a hydrogen consumption of only about 1125 cu. ft. Both types of oils exhibited similar kinetic behavior with activation energies ranging from 14,000 to 16,000 cal./mole. The hydrocracking of coal-based and petroleum oils must be preceded by the hydrotreating of the feed stocks to ensure low coke yield and longer catalyst life. The disadvantages associated with the processing of coal-based oils can be offset by the superior quality of their products, thereby affecting the overall processing almost similar to petroleum oils.

Introduction

Hydrocracking is employed in the petroleum industry, in recent years, for the processing of different types of feed stocks (Craig and Forster, 1966; Durr, 1967). It was also applied as a potential method for the refining of coal-derived liquids (Alpert, et al., 1966, Katsobashvili and Elbert,

1966). The hydrocracking of coal-based oils differs to some extent from petroleum oils since the former contain larger quantities of oxygenated compounds and aromatic hydrocarbons. In view of the anticipated shortage of crude petroleum, the petroleum refineries may have to augment their feed stocks with synthetic oils and process them in the existing equipment. The additional oil requirements may be met in the near future from coal liquification processes and, hence, it is necessary and useful to understand the fundamental differences that may exist between the refining of petroleum and coal-based oils. Hydrocracking is a versatile processing method and it may be valuable to study and compare the behavior of petroleum and coal-based oils under hydrocracking conditions. The fundamental aspects of hydrocracking of petroleum and coal-based oils are not well understood at the present time though some work was earlier reported mainly on the study of product distributions or catalyst performance (Carpenter, et al., 1963; Archibald, et al., 1960). Some data, however, were reported on the mechanism of hydrocracking of some pure hydrocarbons (Archibald, et al., 1960; Flinn, et al., 1960). In the present communication, the results of hydrocracking of three petroleum fractions and two coal-based oil fractions are reported. A comparison was made between the petroleum and coal-based oils with respect to their behavior under hydrocracking conditions.

Experimental

Materials.

The petroleum fractions were obtained from a mixed base crude oil by atmospheric distillation. The coal oil was obtained from a high volatile bituminous coal by hydrogenation in an entrained bed reactor unit at 2000 p.s.i. pressure and 510°C with stannous chloride as the catalyst. Low

temperature tar was prepared from the same coal in a laboratory oven at 580°C. The coal oil and tar fractions were obtained by distillation of the whole oils, respectively. The hydrorefining catalyst contained 3% cobalt oxide and 12% molybdenum trioxide supported on alumina in the form of pellets of 0.083-inch diameter and 0.125-inch height with a surface area of 210 sq. meters per gram. The hydrocracking catalyst contained 6% nickel sulfide and 19% tungsten disulfide supported on silica-alumina in the form of pellets of 0.083-inch diameter and 0.125-inch height with a surface area of 198 sq. meters per gram.

Equipment.

The hydrocracking unit (Figure 1) contained a vertical tubular stainless steel reactor of 0.75-inch inside diameter and 40-inch length with precision equipment for controlling temperature, pressure, and gas and liquid flow rates. The reactor was heated uniformly by a tubular ceramic furnace of 1.5-inch inside diameter and 38-inch length. The first 20-inch length of the reactor from the top was packed with ceramic beads of 0.17-inch diameter, the next 6.5 inches with the catalyst (60 c.c), and the following 12 inches again with ceramic beads. The temperature of the catalyst bed was maintained constant and the reaction temperature was measured by a thermocouple placed at the center of the catalyst bed. The hydrogen supply was taken from hydrogen tanks. The hydrorefining was also done in the same unit but with the refining catalyst.

Hydrocracking procedure.

The whole system was first flushed with hydrogen to remove air, pressurized, and heated to the reactor temperature. The pressure was then adjusted to the experimental pressure and the oil was fed at the desired rate. The

initial one hour was taken as an offstream period for bringing the reactor and the product recovery system to equilibrium. The hydrogen to oil feed ratio was maintained at about 500. The values of space velocities varied in the range of $\pm 10\%$ and were rounded off. The product was cooled in the condenser and the liquid product was collected in the separator. The gaseous product containing some uncondensed oil was passed through an active carbon tower to adsorb the oil and a gas meter to measure the rate and total volume passed. Several gas samples were withdrawn during each experiment for analysis. The difference in the weight of active carbon before and after the experiment was taken as the amount of uncondensed naphtha. The yield of the liquid product varied between 95 and 100% with an initial boiling point between 50° and 65°C . The yield of gas and each hydrocarbon component of the gas were calculated from the total gas and its composition. The liquid product was distilled and the fraction boiling up to 200°C was designated as naphtha. The fraction boiling up to 100°C was designated as light naphtha and the fraction boiling from 100° to 200°C as heavy naphtha. The hydrotreating was also done in a similar manner at 1500 p.s.i. pressure, 425°C , and 1-space velocity. All the products reported are double-pass products and the product distribution data were obtained at a space velocity of about 0.5. Cumene was hydrocracked over the fresh catalyst and also intermittently during the experimental work to test the activity of the catalyst. The catalyst was either regenerated or replaced by fresh catalyst when the activity with respect to cumene cracking fell by about 5 percentage points.

Coke determination.

The used catalyst was taken out from the reactor and dried at 110°C for two hours to remove moisture and volatile hydrocarbons. Twenty-five grams of

the dried catalyst was packed in a glass tube of 0.5-inch internal diameter and 12-inch length heated to 600°C by a tubular furnace. A stream of air was passed through the tube at the rate of about 15 c.c per minute and the effluent was passed through a furnace containing cupric oxide at 700°C to oxidize carbon monoxide to carbon dioxide, a tower containing Drierite to adsorb any moisture and a tower of Ascarite to adsorb carbon dioxide. The carbon on the catalyst was calculated from the weight of carbon dioxide and reported as coke. The catalyst deposit was not strictly carbon but coke containing both carbon and hydrogen. The coke values reported actually refer to the carbon content of the coke, the latter amounting to about 95% of the former, the remaining being hydrogen.

Product analysis.

All the analyses of the liquid products were done by ASTM and other standard methods and gaseous products by gas chromatographic and mass spectrometric methods (Qader and Hill, 1969).

Results and Discussion

The yield of naphtha from petroleum fractions increased linearly with the reaction temperature. The stove, diesel, and gas oils yielded a maximum of 79, 78, and 77% naphtha at 1500 p.s.i. pressure and 79, 80, and 79% at 2000 p.s.i. pressure and 500°C, respectively. Increasing the reaction pressure from 1500 to 2000 p.s.i. did not change the naphtha yield to any appreciable extent (Figure 2). On the other hand, the naphtha yield from coal-based oils was increased significantly with an increase in the hydrogen pressure. The coal oil and low temperature tar yielded a maximum of 63 and 60% naphtha at 1500 p.s.i. pressure and 79 and 77% at 2000 p.s.i. pressure and 500°C, respectively. The yield of naphtha did not vary linearly with temperature at 1500 p.s.i. pressure while it was linear at a pressure of 2000 p.s.i. The effect was more pronounced at temperatures above 450°C (Figure 3). The results

indicate that the hydrocracking of coal-based oils needs higher hydrogen pressures when compared to the petroleum oils and both types of oils affect almost similar naphtha yields at a pressure of 2000 p.s.i. In case of coal oils, the higher hydrogen pressure is needed for the hydrogenation of aromatic hydrocarbons and the heterocyclic compounds. At pressures of 2000 p.s.i. and above, the petroleum and coal oils exhibit similar behavior under hydrocracking conditions.

The API gravity and the characterization factor of a liquid fuel mainly depend upon its boiling range and the aromatic hydrocarbon content. In case of petroleum oils investigated, the characterization factor increased with a decrease in gravity (Figure 4) which appears to be mainly due to the differences in the boiling ranges of the feed stocks since they have similar composition (Table 1). Though a similar relationship was exhibited by coal-based oils (Figure 4), the factors contributing to such a behavior seem to be different. While the lower gravity of the coal oil when compared to coal tar may be due to the differences in the boiling ranges and aromatic contents of the oils, the high characterization factor of the coal oil does not seem to commensurate with a slight difference in the boiling range and the aromatic hydrocarbons. The characterization factor might have been influenced by the presence of higher concentrations of hydroaromatics in the coal oil. This is further evidenced by the higher naphtha yield from coal oil at 1500 p.s.i. pressure (Figures 5 and 6) where the hydrogenation of aromatics to the corresponding hydroaromatics which undergo subsequent cracking does not occur to any appreciable extent (Qader, et al., 1968). However, hydrogenation of aromatics to the corresponding hydroaromatics does take place at a pressure of 2000 p.s.i., thereby narrowing down the gap between naphtha yields from coal oil

and coal tar fractions as shown in Figures 5 and 6. The increase in the yield of naphtha with gravity and the decrease with characterization factor of petroleum fractions (Figures 5 and 6) are mainly due to the differences in their boiling ranges.

The product distribution data indicated that the hydrocracking of petroleum fractions produces higher quantities of gaseous product when compared to coal-based oils at all levels of naphtha formation (Figure 7). Coal-based oils produced more C_1 - C_3 hydrocarbons than petroleum oils at different levels of butane production (Figure 8). The production of $+200^\circ\text{C}$ oil fraction was higher in the hydrocracking of coal-based oils. However, the differences are not large enough to alter the product distribution significantly. Isomerization is an important aspect of hydrocracking and the results shown in Figure 9 indicated the occurrence of more isomerization in the hydrocracking of petroleum oils when compared to the coal-based oils at all levels of naphtha formation. The iso-normal ratios in butanes varied between 1 and 4 in the case of petroleum oils, while the ratios varied between 1 and 2.75 in the case of coal-based oils. Occurrence of isomerization during hydrocracking produces better quality naphtha and this is an advantage associated with the petroleum oils under hydrocracking conditions. However, there may be several other factors which influence the quality of naphtha. The relative proportions of light and heavy fractions of naphtha will also contribute to the overall quality of the naphtha. Normally light naphthas produced from petroleum fractions have higher octane ratings than heavy naphthas, necessitating the subsequent reforming of heavy naphtha. The results in Figures 10 and 11 indicated that petroleum oils produce more light naphtha relative to heavy naphtha when compared to coal-based oils. The ratios of heavy-light naphthas varied

between 2 and 4 in the case of petroleum oils, while the ratios varied between 3.5 and 4.5 in the case of coal-based oils. This is again an added advantage associated with petroleum oils, though this is not the final deciding factor.

The hydrocarbon composition of naphthas obtained from petroleum and coal-based oils was shown in Figure 12. Coal-based naphthas contained higher proportions of aromatic hydrocarbons than petroleum naphthas. At about 80% formation, petroleum naphthas contained about 35 to 40%, while coal-based naphthas contained about 55% aromatic hydrocarbons. This may make a great difference in the octane rating of the naphthas and coal-based naphthas are expected to have high octane values. Petroleum naphthas contained slightly higher concentrations of naphthenes and isoparaffins than coal-based naphthas, while the contents of normal paraffins and olefins were almost the same in both cases. The quality of coal-based naphthas was found to be much superior to the petroleum naphthas, as shown in Figure 13. The clear research octane numbers of coal-based naphthas varied between about 80 to 90, while the octane numbers of the petroleum naphthas varied only in between about 65 to 80. At the maximum yield of about 80%, coal-based naphthas had clear research octane numbers of about 90, while the octane ratings were below 80 numbers in the case of petroleum naphthas. The coal-based naphthas can be used as regular grade gasoline without further treatment and as premium grade product simply by the use of additives. Petroleum naphthas need to be reformed before they can be used either as regular or premium grade materials. Coal-based naphthas have slightly higher concentrations of sulfur and nitrogen which, however, are much below the specified limits.

Hydrogen requirement is an important factor which contributes significantly to the overall refining cost of fuel oils. The results shown in Figure 14

illustrated that hydrogen consumption was high in the hydrocracking of coal-based oils when compared to petroleum oils. At the maximum yield of about 80% naphtha, hydrogen consumption varied between 800 to 1100 and 1500 to 1600 cu. ft. per barrel of feed stock in the hydrocracking of petroleum and coal-based oils, respectively. The high hydrogen consumption in the case of coal-based oils was due to the hydrogenation of aromatic hydrocarbons and heterocyclic compounds, especially the oxygenated compounds. This is one of the disadvantages associated with the refining of coal-based oils.

Kinetics

For the kinetic study the gas oil and coal oil fractions were used and the hydrocracking experiments were conducted at a constant hydrogen pressure of 2000 p.s.i. The overall rates of hydrocracking were studied by the application of Equation 1 assuming first-order kinetics (Qader and hill, 1969).

$$\ln \frac{X_i}{X_f} = k \frac{1}{\text{LHSV}} \quad (1)$$

where

X_i = initial concentration of the reactant, wt. %

X_f = final concentration of the reactant, wt. %

LHSV = liquid hourly space velocity, volume of liquid feed per hour per volume of catalyst

k = specific reaction rate constant

The plots of reciprocal space velocity versus $\log \frac{X_i}{X_f}$ are shown in Figures 15 and 16. The plots were linear and, thus, the first-order rate constants can be represented by Equations 2 and 3.

$$-\frac{d(\text{gas oil})}{dt} = k_g (\text{gas oil}) \quad (2)$$

$$-\frac{d(\text{coal oil})}{dt} = k_c (\text{coal oil}) \quad (3)$$

where k_g and k_c are rate constants for gas oil and coal oil hydrocracking, respectively. The Arrhenius plots (Figure 17) were linear and the rate constants were found to be represented by Equations 4 and 5.

$$k_g = 0.3651 \times 10^4 e^{-14,300/RT} \text{ hr.}^{-1} \quad (4)$$

$$k_c = 0.8395 \times 10^4 e^{-15,500/RT} \text{ hr.}^{-1} \quad (5)$$

The following values of enthalpies and entropies of activation were calculated from plots of $\log \frac{k}{T}$ versus $\frac{1}{T}$ by applying Eyring equation (Figure 18).

$$\Delta H_g^\ddagger = 12,800 \text{ cal./mole}, \quad \Delta S_g^\ddagger = -52 \text{ e.u.}$$

$$\Delta H_c^\ddagger = 1,400 \text{ cal./mole}, \quad \Delta S_c^\ddagger = -50 \text{ e.u.}$$

The kinetic data indicates that both the gas oil and coal oil exhibit similar kinetic behavior under hydrocracking conditions except the coal oil needs a slightly higher activation energy. The mechanisms of hydrocracking of gas oil and the coal oil appear to be similar as proposed earlier and the energetics suggest that chemical reactions involving the cracking of C-C, C-O, C-S, and C-N bonds will control the reaction rate (Qader, et al., 1968 and 1969). The catalyst used in this investigation is a dual-functional one, containing both a cracking component and a hydrogenation component. Since cracking is the rate controlling step in hydrocracking, the reaction rates and the product yields are mainly influenced by the activity of the cracking component of the catalyst. Therefore, it is essential to carry out the hydrocracking process under conditions wherein the cracking component maintains high activity. The cracking activity of the catalyst is due to the acidic surface sites of silica which may get poisoned due to the accumulation of coke and the basic nitrogen compounds. The coke formation may also reduce the activity of the hydrogenation component of the catalyst. Therefore, it is important to study the coke deposition on the catalyst during hydrocracking. Figure 19 shows the coke

deposition on the catalyst by the hydrocracking of gas oil and coal oil at a temperature of 480°C, 2000 p.s.i. pressure, and 1-space velocity. The coke formation by the coal oil was almost double the amount by the gas oil, which suggests that the catalyst life will be shortened to a great degree during the hydrocracking of coal oil. This may make the hydrocracking of coal oil more expensive when compared to the gas oil. However, if the feed stocks are hydrorefined in a preceding step to remove the nitrogen compounds which otherwise will poison the acidic sites of the cracking component of the catalyst during hydrocracking, the coke formation on the catalyst can be reduced to a great extent as shown in Figure 20. Further, the gas oil and the coal oil affect almost the same amount of coke deposition on the catalyst during the hydrocracking of the hydrorefined feed stocks. The results suggest that the hydrocracking of either petroleum or coal-based oils on the dual-functional catalyst must be preceded by the hydrorefining of the feed stocks and the hydrocracking of the preredefined feed stocks will exhibit similar characteristics with respect to catalyst requirements. This investigation indicates that though the hydrocracking of petroleum oils has certain advantages over the coal-based oils, the disadvantages associated with the latter may be offset by the superior quality of their products, thereby affecting the overall processing of both types of oils almost similarly.

Table 1. Properties of feed materials.

	Stove oil	Diesel oil	Gas oil	Coal oil fraction	Low tem- perature tar fraction
Gravity, °API	38.2	36.5	32.4	21.5	23.4
Characterization factor	11.2	11.6	11.9	9.9	9.5
Sulfur, wt. %	0.24	0.22	0.38	0.62	0.84
Nitrogen, wt. %	0.18	0.16	0.14	0.42	0.58
Oxygen, wt. %	Nil	Nil	Nil	3.6	4.8
Distillation					
I.B.P., °C	200	250	350	200	200
50%	250	302	430	238	260
F.B.P., °C	300	380	490	370	360
Hydrocarbon analysis, vol. %					
Saturates	80	80	81	38	28
Aromatics	20	20	19	57	54
Olefins	Nil	Nil	Nil	5	18

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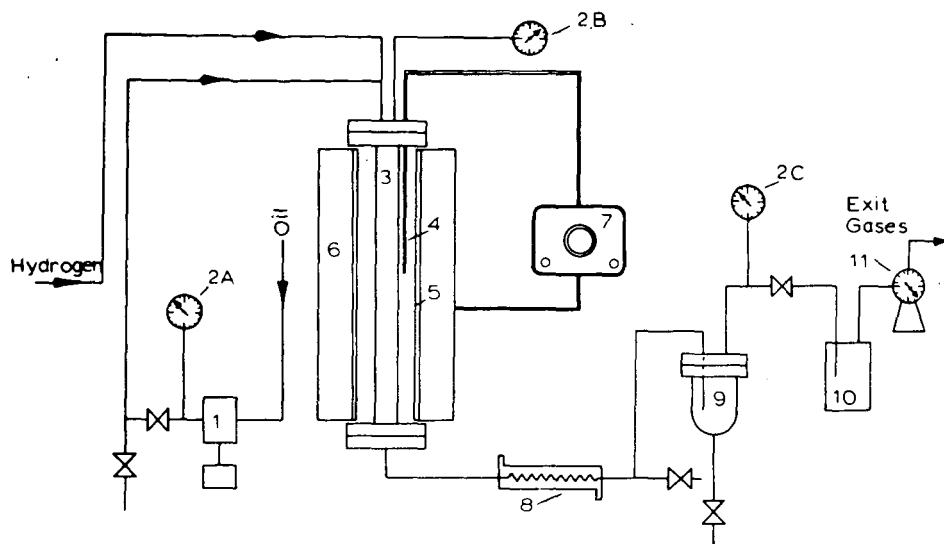
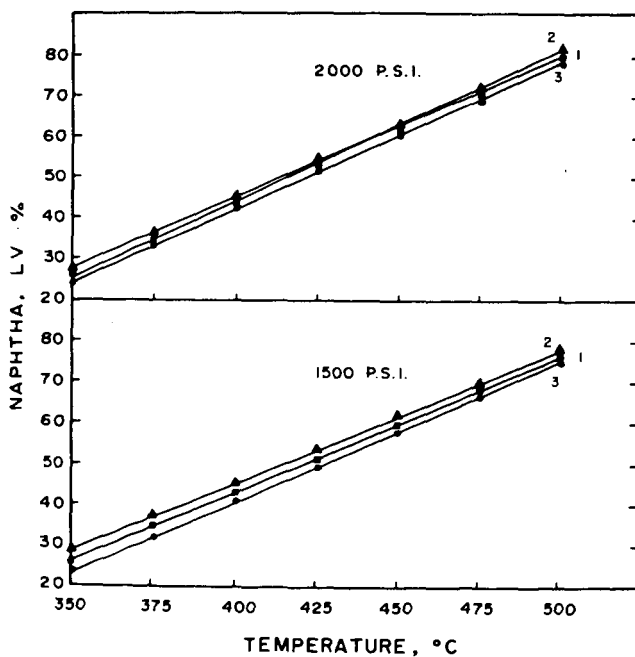


FIGURE 1. FLOW SHEET OF THE HYDROTREATING UNIT.

1. HIGH PRESSURE PUMP, 2A, 2B, 2C. PRESSURE GAUGE, 3. REACTOR, 4. THERMOCOUPLE, 5. CERAMIC FURNACE, 6. INSULATION, 7. TEMPERATURE CONTROLLER, 8. CONDENSER, 9. SEPARATOR, 10. ACTIVE CARBON TOWER, 11. GAS METER.

FIGURE 2. INFLUENCE OF TEMPERATURE AND PRESSURE ON NAPHTHA YIELD.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL.

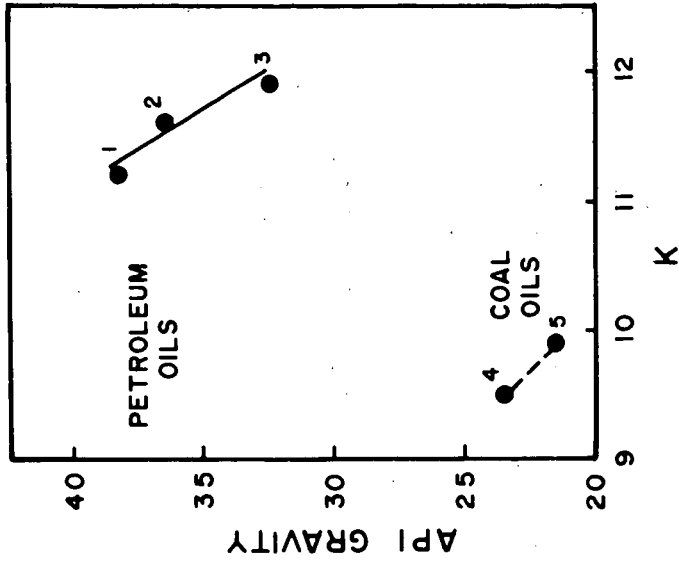


FIGURE 4. RELATIONSHIP BETWEEN GRAVITY AND CHARACTERIZATION FACTOR.

1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

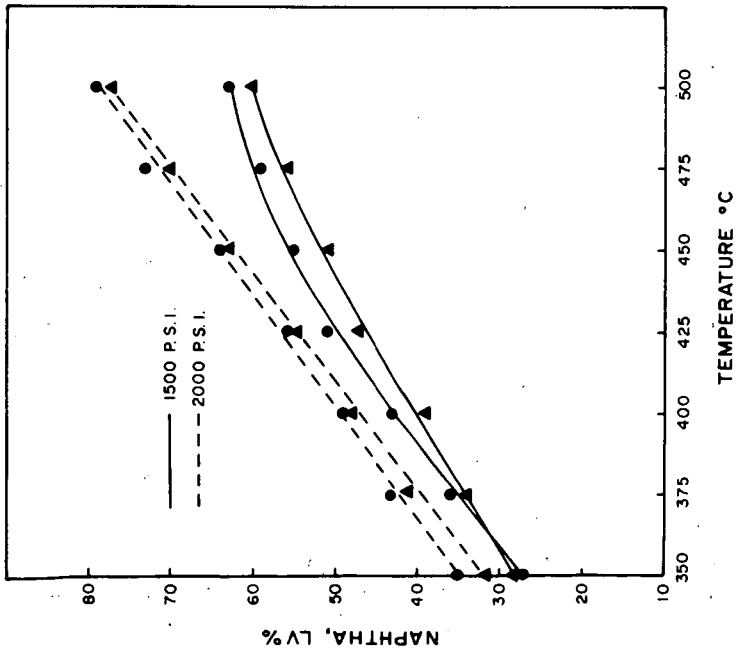


FIGURE 3. INFLUENCE OF TEMPERATURE AND PRESSURE ON NAPHTHA YIELD.

1. COAL OIL, 2. LOW TEMPERATURE TAR.

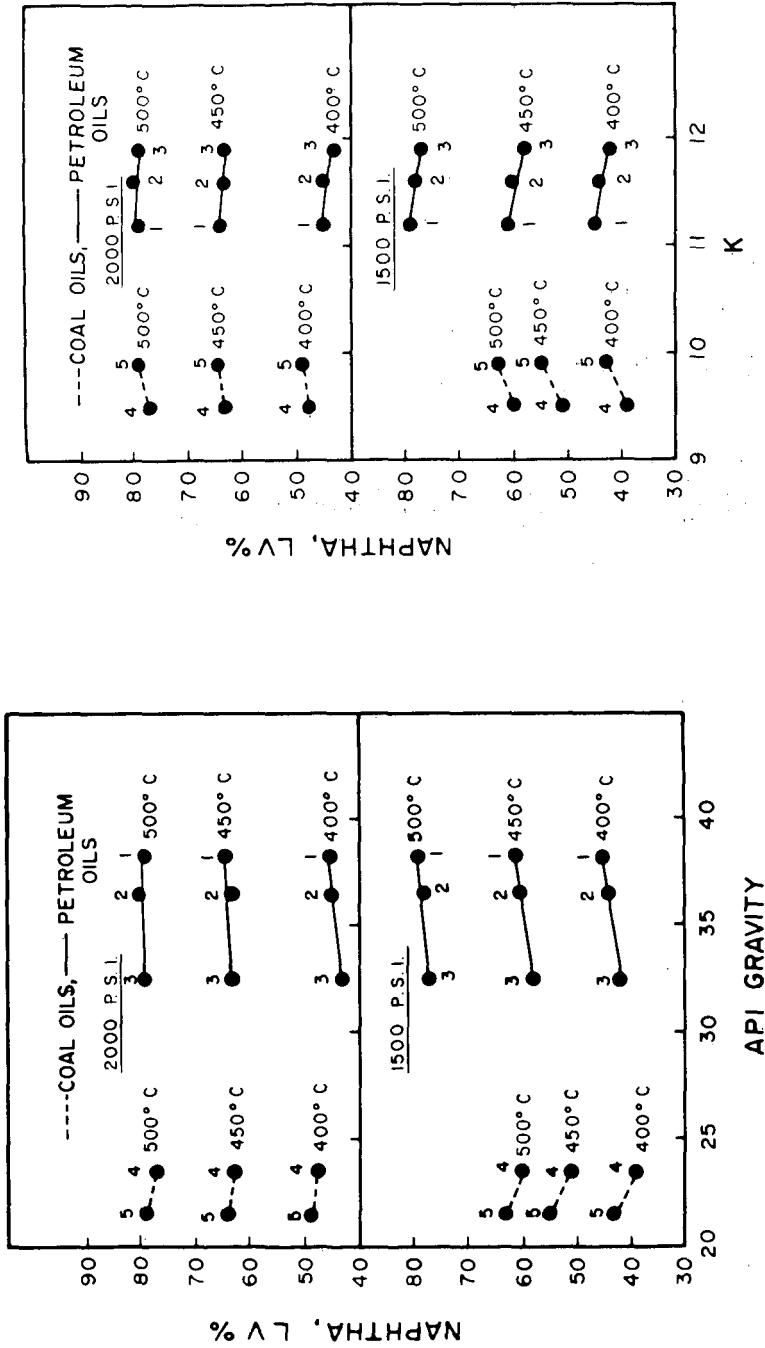


FIGURE 5. RELATIONSHIP BETWEEN NAPHTHA YIELD AND GRAVITY OF FEED STOCKS.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

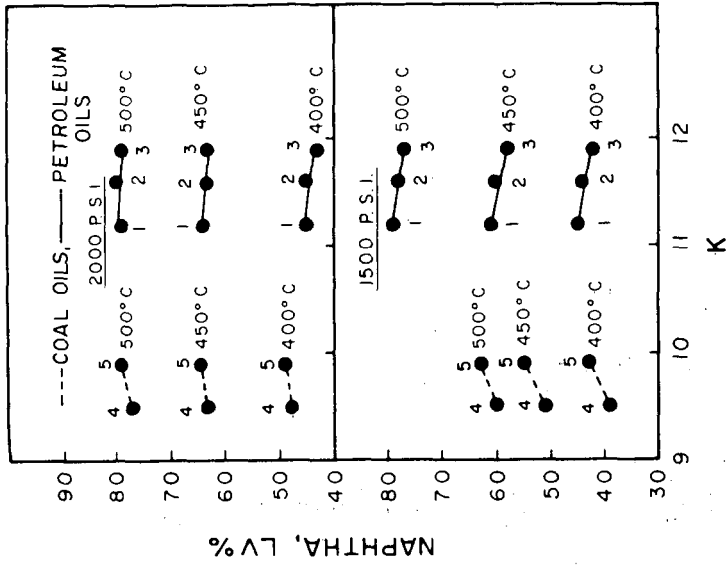


FIGURE 6. RELATIONSHIP BETWEEN NAPHTHA YIELD AND TEMPERATURE.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

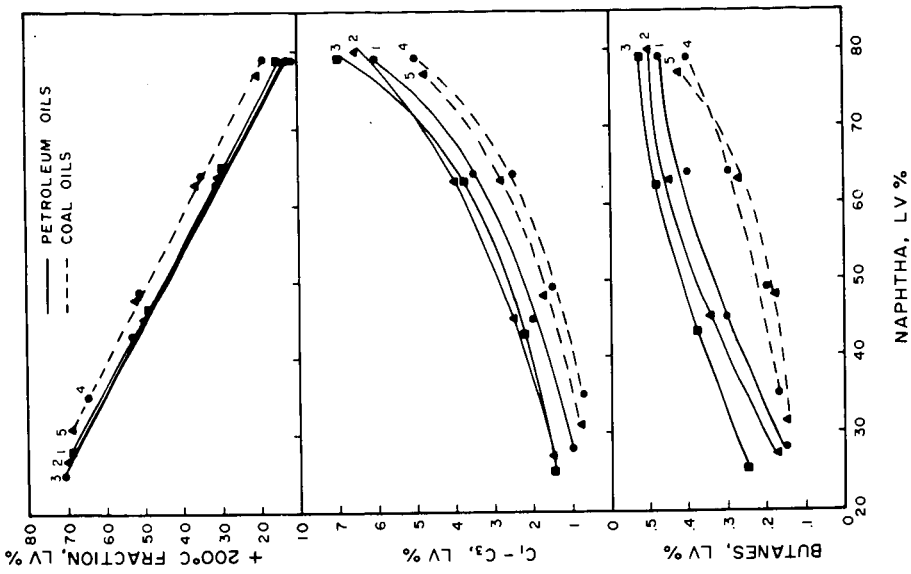


FIGURE 7. PRODUCT DISTRIBUTION AT DIFFERENT LEVELS OF NAPHTHAM YIELD.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

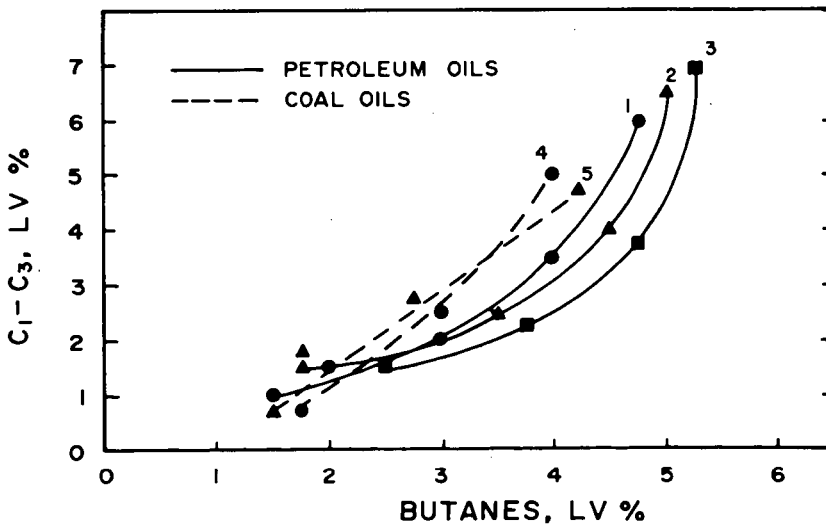


FIGURE 8. RATIO OF BUTANES AT DIFFERENT LEVELS OF NAPHTHAM YIELD.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

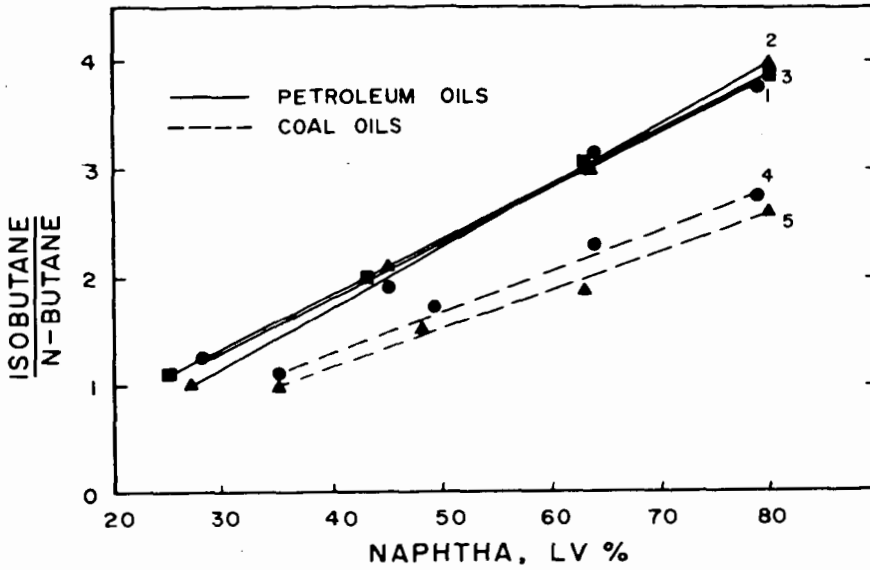


FIGURE 9. RELATIONSHIP BETWEEN THE FORMATION OF C_1-C_3 HYDROCARBONS AND BUTANES.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

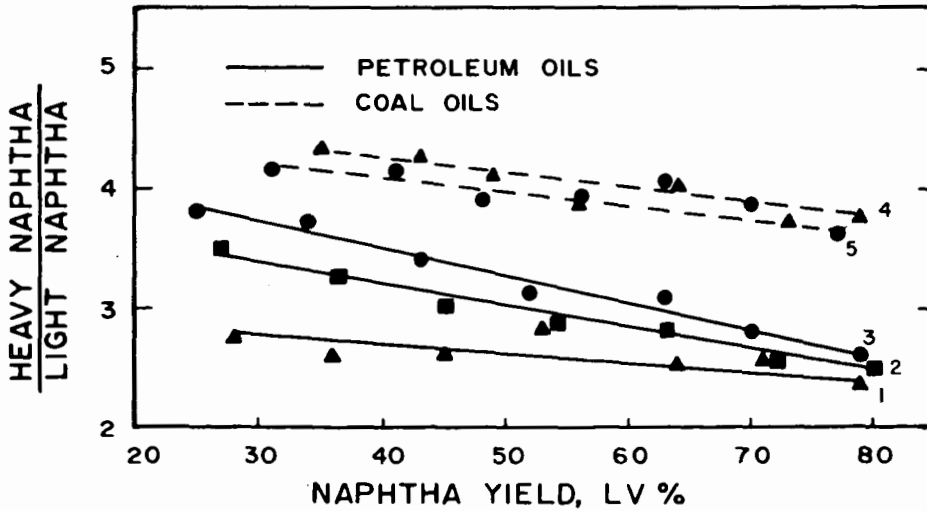


FIGURE 10. RATIO OF LIGHT AND HEAVY NAPHTHA AT DIFFERENT LEVELS OF CONVERSION.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

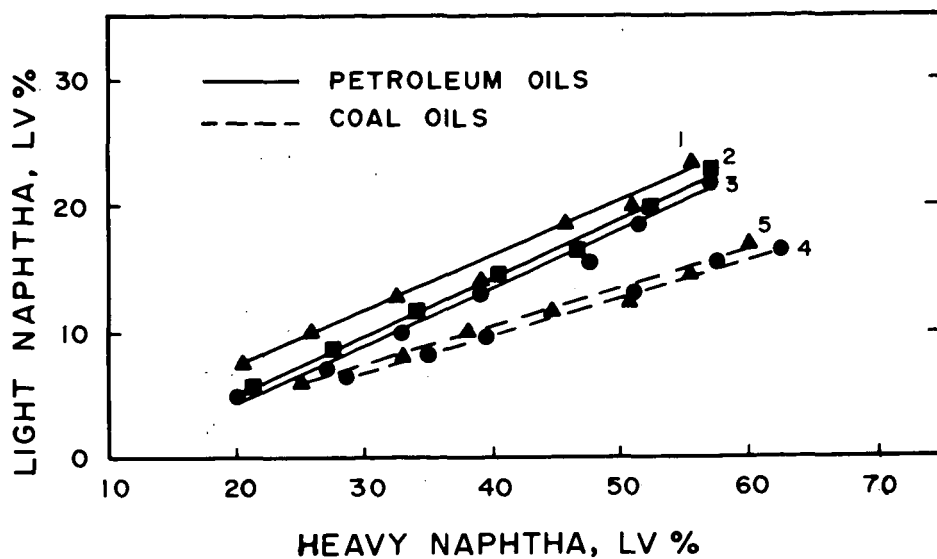


FIGURE 11. RELATIONSHIP BETWEEN THE FORMATION OF LIGHT AND HEAVY NAPHTHA.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR,
5. COAL OIL.

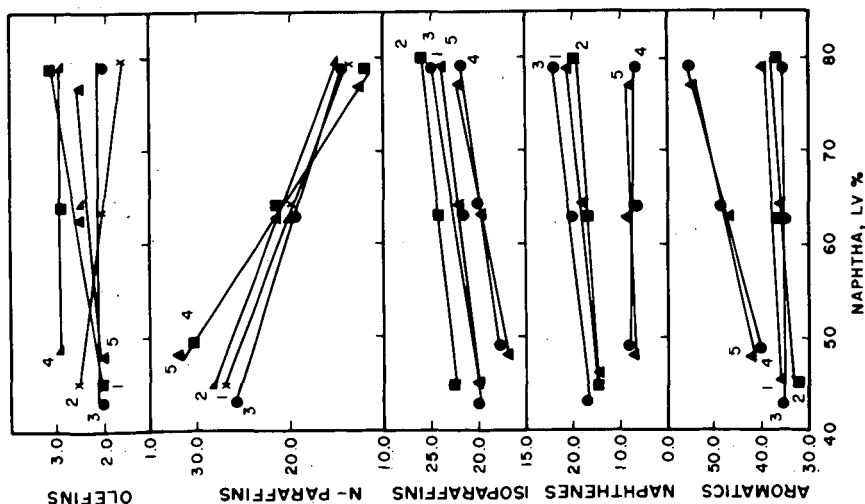


FIGURE 12. COMPOSITION OF NAPHTHA AT DIFFERENT LEVELS OF FORMATION.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

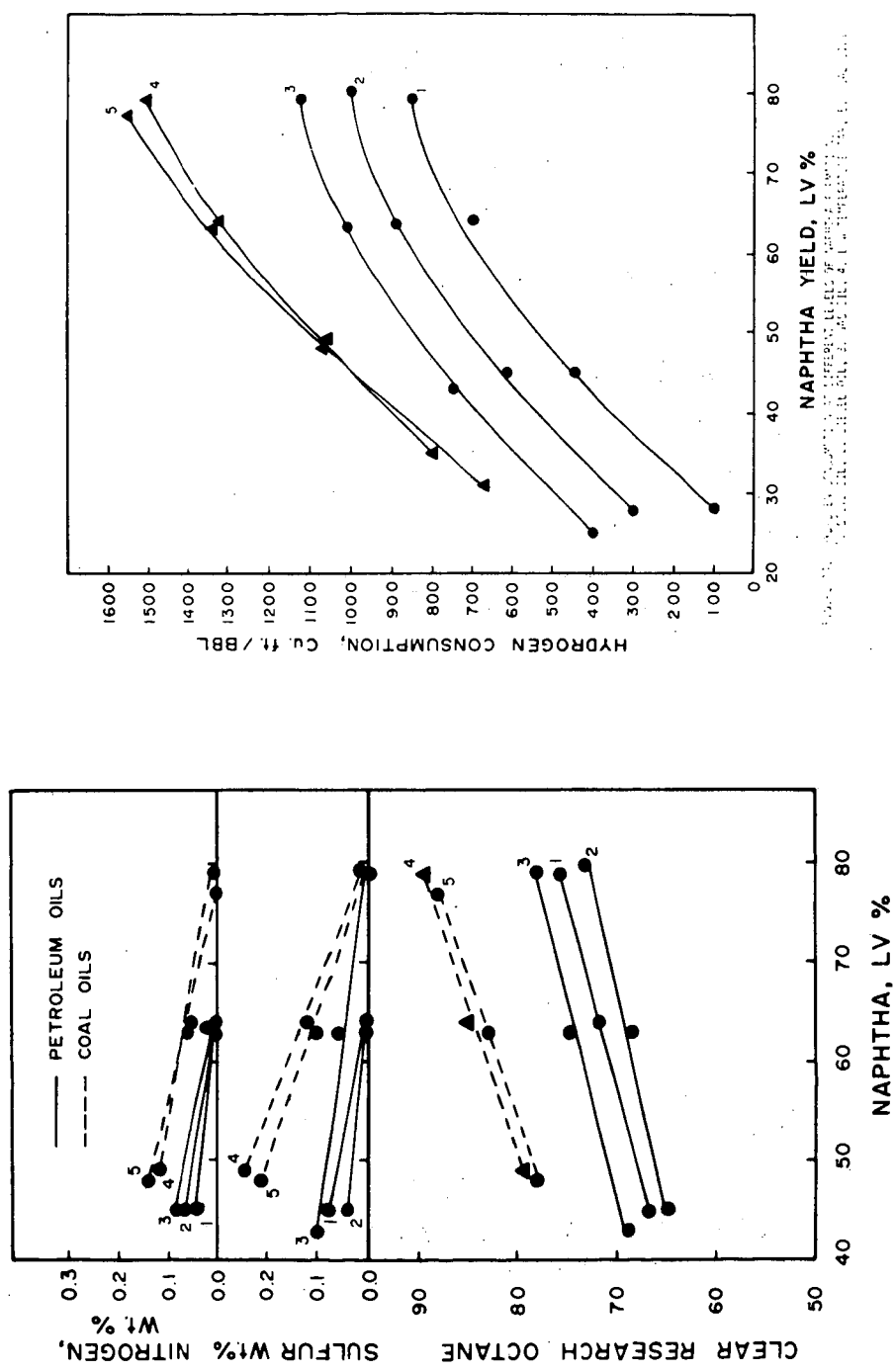


FIGURE 13. QUALITY OF NAPHTHA AT DIFFERENT LEVELS OF FORMATION.
1. STOVE OIL, 2. DIESEL OIL, 3. GAS OIL, 4. LOW TEMPERATURE TAR, 5. COAL OIL.

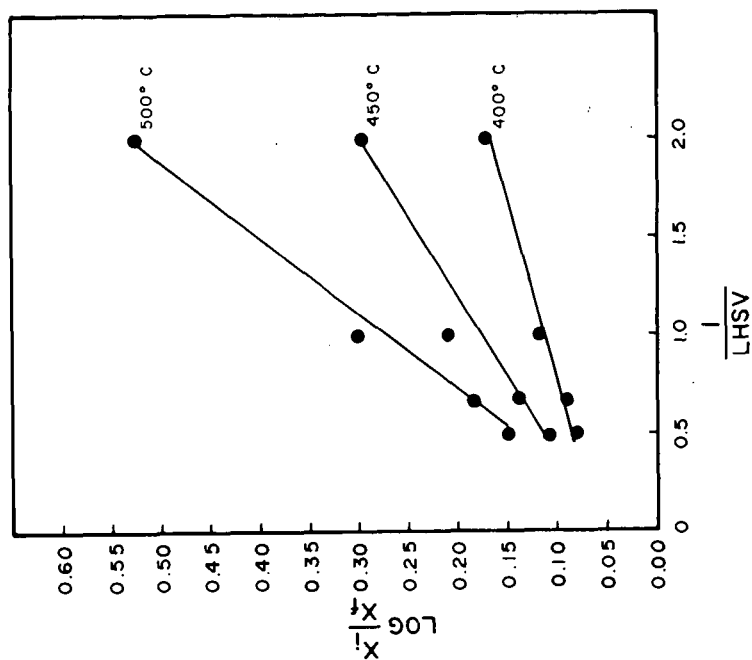


FIGURE 16. FIRST-ORDER PLOT FOR HYDROCRACKING OF COAL OIL.

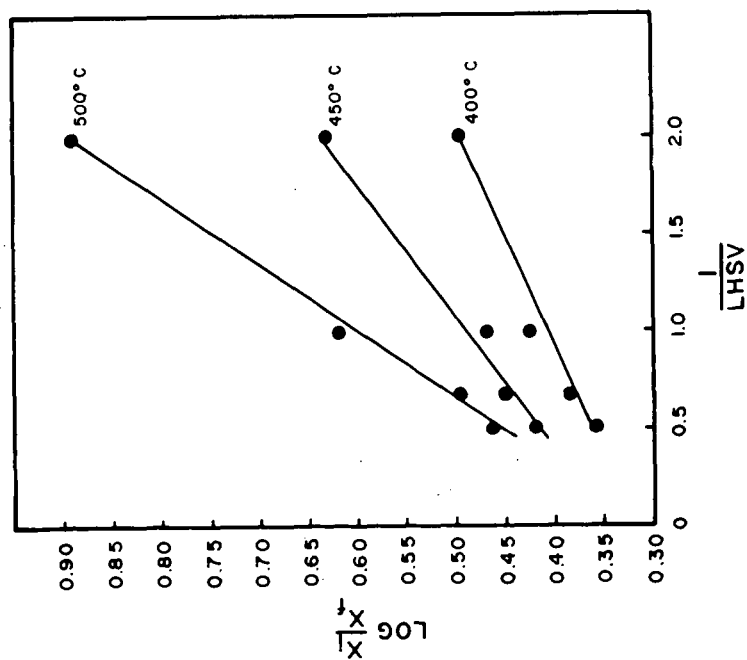


FIGURE 15. FIRST-ORDER PLOT FOR HYDROCRACKING OF GAS OIL.

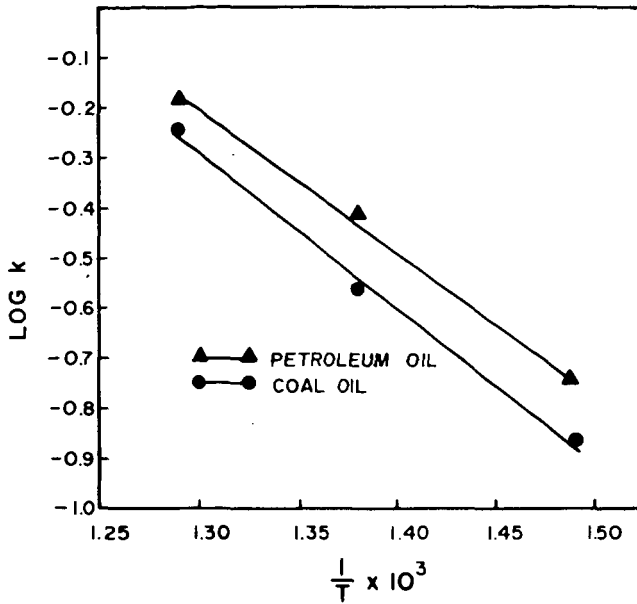


FIGURE 17. ARRHENIUS PLOT FOR HYDROCRACKING OF GAS OIL AND COAL OIL.

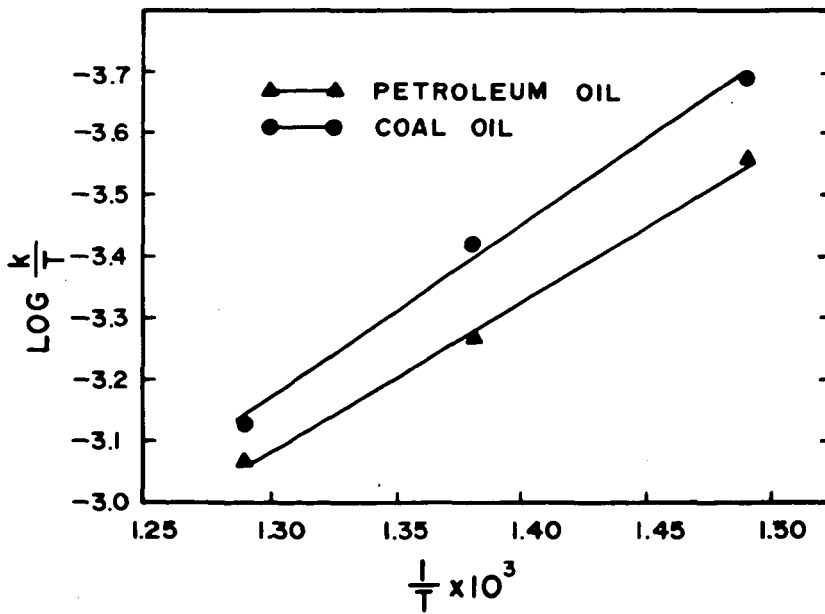


FIGURE 18. EYRING PLOT FOR HYDROCRACKING OF GAS OIL AND COAL OIL.

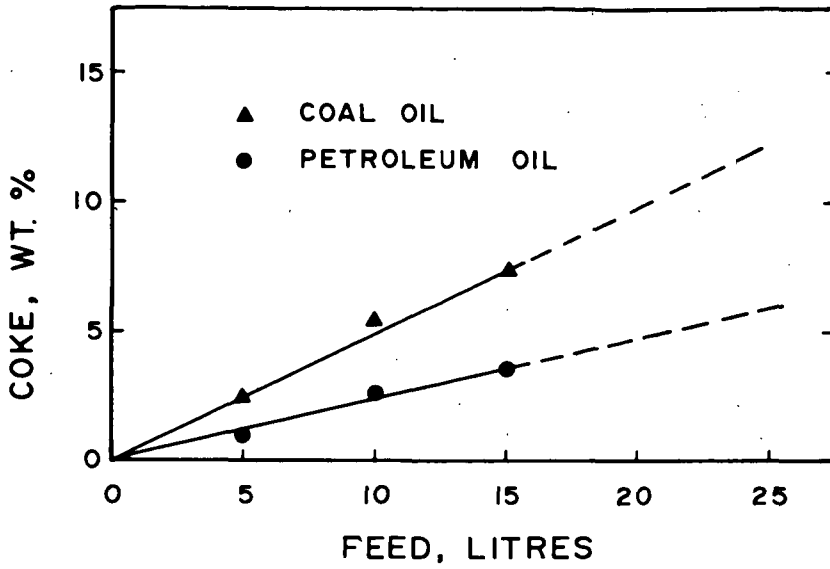


FIGURE 19. COKE FORMATION DURING HYDROCRACKING OF GAS OIL AND COAL OIL.

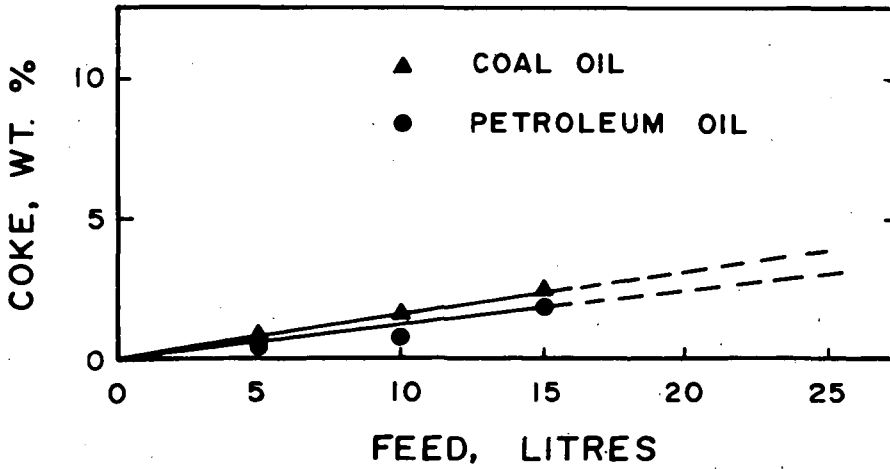


FIGURE 20. COKE FORMATION DURING HYDROCRACKING OF REFINED GAS OIL AND COAL OIL.